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AMRA TR 63-01

SOME CALCULATIONS OF OBSERVABLES BASED ON THE SCHWARTZ METHOD

by

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MATERIALS RESEARCH LABORATORIES

U. S. ARMY MATERIALS RESEARCH AGENCY

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Atomic and molecular physics

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ABSTRACT

C. Schwartz has derived an improved method for the calculation of observables other than the energy utilizing approximate wave functions. We have extended his calculations for the ground state of helium to other one electron observables such as the X-ray scattering factor, $<1/r^2>$, $<r>$ and to $<\delta(r)>$ for the triplet state of helium.

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*Work performed while a guest of the Department of Mathematics, Imperial College, London, under a Secretary of the Army's Research and Study Fellowship.

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Schwartz[1] has suggested that the solution of the equation

$$[F, H]\Psi_o = \Omega\Psi_o - \langle\Omega\rangle\Psi_o \tag{1}$$

(where Ω is an operator whose expectation value is sought, Ψ_o a trial wave function, H the hamiltonian of the system, and $\langle\Omega\rangle$ the expectation value of Ω evaluated with Ψ_o) leads to a corrected value of $\langle\Omega\rangle$ (denoted $\langle\Omega\rangle^*$) given by

$$\langle\Omega\rangle^* = \langle\Omega\rangle + 2(\Psi_o,\ F(H - \langle E\rangle)\ \Psi_o) \tag{2}$$

whose error is approximately the error in the expectation value of the energy $\langle E\rangle$ where

$$\langle E\rangle = (\Psi_o,\ H\Psi_o) \tag{3}$$

If the Schwartz equations are correct this would yield a marked improvement in the error of observables (other than the energy) calculated from wave functions obtained by traditional methods like Hartree, Hartree-Fock, etc. Schwartz justified his method by evaluating certain observables for the ground state of helium. We have extended his calculations for the ground state of helium to other one electron observables such as the X-ray scattering factor, $\langle 1/r^2\rangle$, $\langle r\rangle$ and to $\langle\delta(r)\rangle$ for the triplet state of helium all with remarkable success.

Table I summarizes the results for the ground state of helium employing the trial wave function

$$\Psi_o = \frac{b^3}{\pi} e^{-br_1} e^{-br_2} \; ; \text{ (singlet)}$$
$$b = \frac{me^2}{\hbar^2} (Z - \frac{5}{16}) \tag{4}$$

TABLE I

Comparison of Various Calculations on the Ground State of Helium

(All in atomic units except $\sin\theta/\lambda$ in $\mathring{A}^{-1}$)

	Pekeris[2]	% Error	Hartree-Fock	% Error	Schwartz	% Error
Energy	-2.904	-	-2.8615	1.12	-2.843	2.1
$<\delta(r_1)>$	*22.75	-	8.88	90	22.95	1
$<r_1^2>$	1.1935	-	1.172	1.8	1.161	2.7
$<r_1>$	.9295	-	.924	0.6	.920	1.0
$<\frac{1}{r_1}>$	1.688	-	1.691	0.18	1.681	0.05
$<\frac{1}{r_1^2}>$	6.0134	-	6.02	0.05	6.035	0.3

$(\sin\theta/\lambda)$	Hylleras[4]**		Hartree-Fock		Schwartz	
	$<f>$	% Error	$<f>$	% Error	$<f>$	% Error
0.1	1.838	-	1.834	0.2	1.841	0.2
0.2	1.461	-	1.464	0.2	1.464	0.2
0.3	1.061	-	1.066	0.4	1.062	0.1
0.4	.739	-	.741	0.3	.7375	0.2
0.5	.509	-	.512	0.6	.506	0.6
0.6	.354	-	.355	0.3	.351	0.8
0.7	.249	-	.2494	0.2	.247	0.8
0.8	.178	-	.1763	0.2	.177	0.6
0.9	.129	-	.130	0.7	.129	0.0
1.0	.0953	-	.0976	2.4	.0946	0.7

*Kinoshita value[3]

**(Error in E (.25%))

The X-ray scattering factor can be evaluated in closed form for the two electron systems H^-, He, Li^+, Be^{++}, etc., and is given by

$$f = f_o + \Delta$$

$$f_o = \frac{2}{\left(1 + \frac{k^2}{4b^2}\right)^2}$$

$$\Delta = \frac{f_o}{32Z-10}\left\{\frac{10-\frac{15k^2}{2b^2}}{1+\frac{k^2}{4b^2}} - \frac{4-\frac{17k^2}{8b^2}-\frac{5k^4}{64b^4}}{\left(1+\frac{k^2}{16b^2}\right)^2} + \left(\frac{6k}{b}-\frac{24b}{k}\right)\tan^{-1}\left(1+\frac{k/4b}{8b^2}\right) + 12\ln\left(\frac{1+\frac{k^2}{4b^2}}{1+\frac{k^2}{16b^2}}\right)\right\} \qquad (5)$$

$k = 4\pi\sin\theta/\lambda$ (in Bohr units; divide by 6.65 to convert to $\sin\theta/\lambda$ in Å^{-1}). Table I also lists the values of the observables obtained from the Hartree-Fock wave function and while it gives good results for most observables it deviates appreciably for $\langle\delta(r)\rangle$. Table I clearly shows that the errors in the Schwartz method are <u>always</u> comparable to the error in the energy.

In the case of the triplet state of two electron atoms the trial wave function (non-determinantal)

$$\Psi_o(1s) = \frac{b^{3/2}}{\pi^{1/2}} e^{-br_1}$$

$$\Psi_o(25) = \frac{b^{3/2}}{\pi^{1/2}} \left(1-\frac{4}{9}br\right) e^{-br_{2/3}} \qquad \text{(triplet)} \qquad (6)$$

$$b = (1.072Z - 0.1235)\ me^2/k^2$$

yields an energy in error by <0.1 percent. For helium this leads to a value $\langle\delta(r_1)\rangle + \langle\delta(r_2)\rangle = 33.16$ which is in error by 0.1 percent compared to the Pekeris[2] value 33.181 (Bohr units).

One restriction that must be placed on the Schwartz method is that the virial theorem be satisfied. This can be seen in Table II where we have plotted the error in $\langle r^2\rangle$ for the ground state of helium as a function of the error in the energy due to a variation in the parameter b in the trial wave function, Eq. 4. It is seen that the error in $\langle r^2\rangle$ quickly exceeds the error in the energy as b is varied from $Z - \frac{5}{16} = 1.688$ to 1.5.

Inasmuch as all the calculations quoted in this paper were obtained in simple closed form it appears desirable to pursue the Schwartz method to many electron systems.

TABLE II

b	$\langle E\rangle$	% Error	$\langle r^2\rangle$	% Error	$\langle V\rangle/\langle k.E.\rangle$
1.688	5.70	1.9	2.322	-2.7	-2.00
1.65	5.685	2.16	2.42	+1.4	-2.04
1.60	5.68	2.20	2.60	+8.9	-2.11
1.55	5.66	2.50	2.78	+16.6	-2.18
1.50	5.62	3.24	2.96	+24.0	-2.25
1.45	5.58	4.0	3.20	+33.6	-2.32
1.40	5.53	4.8	3.44	+44.0	-2.40

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